

Potential energy curves for P_2 and P_2^+ constructed from a strictly N-representable natural orbital functional

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Abstract

The potential energy curves of P_2 and P_2^+ have been calculated using an approximate, albeit strictly N-representable, energy functional of the one-particle reduced density matrix: PNOF5. Quite satisfactory accord is found for the equilibrium bond lengths and dissociation energies for both species. The predicted vertical ionization energy for P_2 by means of the extended Koopmans' theorem is 10.57 eV in good agreement with the experimental data. Comparison of the vibrational energies and anharmonicities with their corresponding experimental values supports the quality of the resultant potential energy curves.

Keywords: Inhomogeneous electron liquids: P_2 and P_2^+ , NOF Theory, Dissociation Energies, EKT, Ionization Energies

In new quantum Monte Carlo calculations (in course of publication), Amovilli and March have studied N_2 and N_2^+ . This work has motivated us to consider P_2 and P_2^+ , but now using the one-particle reduced density matrix (1-RDM) functional theory in its spectral representation, i.e., the natural orbital functional (NOF) theory [1]. As a result, the ground state energy is expressed in terms of natural orbitals and their occupation numbers.

Recent advances [2–4] have led to the formulation of the first strictly N -representable functional known under the acronym PNOF5 [5]. The latter belongs to a series of functionals [6] based on a reconstruction of the two-particle reduced density matrix (2-RDM) in terms of the 1-RDM by ensuring necessary N -representability positivity conditions on the 2-RDM [7]. This functional has proved to give a remarkably accurate description of systems with near-degenerate one-particle states and of homolytic dissociation processes [8–11]. PNOF5 provides a very appealing one-electron picture [12–15], and has been successfully used [16–18] to predict vertical ionization potentials by means of the extended Koopmans’ theorem (EKT) [19–22].

PNOF5 is an orbital-pairing approach that involves coupling each orbital g , below the Fermi level ($g \leq N/2$), with N_g orbitals above it, which is reflected in the sum rule for the occupation numbers, namely,

$$\sum_{p \in \Omega_g} n_p = 1; \quad g = \overline{1, N/2} \quad (1)$$

In eqn. (1), Ω_g is the subspace containing the orbital g and N_g coupled orbitals to it. Moreover, we consider that these subspaces are mutually disjoint ($\Omega_{g1} \cap \Omega_{g2} = \emptyset$), i.e., each orbital belongs only to one subspace Ω_g . The PNOF5 energy for a singlet state of an N -electron system can be cast as

$$E = \sum_{g=1}^{N/2} E_g + \sum_{f \neq g}^{N/2} \sum_{p \in \Omega_f} \sum_{q \in \Omega_g} n_p n_q (2\mathcal{J}_{qp} - \mathcal{K}_{qp}) \quad (2)$$

$$E_g = \sum_{p \in \Omega_g} n_p (2\mathcal{H}_{pp} + \mathcal{J}_{pp}) + \sum_{p, q \in \Omega_g, p \neq q} \Pi(n_p, n_q) \mathcal{L}_{qp} \quad (3)$$

$$\Pi(n_p, n_q) = \begin{cases} -\sqrt{n_p n_q}, & p=g \text{ or } q=g \\ \sqrt{n_p n_q}, & p, q > N/2 \end{cases} \quad (4)$$

where \mathcal{H}_{pp} denotes the one-particle matrix elements of the core-Hamiltonian. $\mathcal{J}_{pq} = \langle pq|pq \rangle$ and $\mathcal{K}_{pq} = \langle pq|qp \rangle$ are the usual direct and exchange integrals, respectively. $\mathcal{L}_{pq} = \langle pp|qq \rangle$

is the exchange and time-inversion integral [23]. In this work, we consider only one orbital coupled to g in each subspace, the so-called perfect pairing.

Fig. 1 shows the calculated values in Hartrees (E_h) of the total ground-state energy as a function of the internuclear distance R , in Å, for the neutral Phosphorous diatomic molecule using the correlation-consistent valence triple- ζ basis set (cc-pVTZ) developed by Woon and Dunning [24]. The dissociation limit corresponds to a two-fold degeneracy with the generation of two doublet atomic states. We note that the equilibrium bond length is given by PNOF5 as $R_e = 1.901$ Å, which compares quite well with the experimental value of 1.893 Å [25]. Besides, we have obtained an excellent agreement for the dissociation energy (D_e). Indeed, the calculated PNOF5 D_e is 117.1 kcal/mol, whereas the experimental mark (118.0 kcal/mol) taken from a combination of Refs. [25] and [26], differs only in 0.9 kcal/mol. It is also remarkable that PNOF5 is able to reproduce the correct integer number of electrons on the dissociated atoms.

We turn next to the NOF results obtained for the positive molecular ion P_2^+ . Our approach for the computation of the energy of the cation as a function of the internuclear distance R , consists of adding the vertical ionization potential (IP) to the previously obtained energy for the neutral dimer at the corresponding R . The vertical electron detachment energy is computed from the EKT formalism. The equation for the EKT may be derived by expressing the wavefunction of the $(N - 1)$ -electron system as the following linear combination

$$|\Psi^{N-1}\rangle = \sum_i C_i \hat{a}_i |\Psi^N\rangle \quad (5)$$

In Eq. (5), \hat{a}_i is the annihilation operator for an electron in the spin-orbital $|\phi_i\rangle = |\varphi_p\rangle \otimes |\sigma\rangle$ ($\sigma = \alpha, \beta$), $|\Psi^N\rangle$ is the wavefunction of the N -electron system, $|\Psi^{N-1}\rangle$ is the wavefunction of the $(N - 1)$ -electron system, and $\{C_i\}$ are the set of coefficients to be determined. Optimizing the energy of the state Ψ^{N-1} with respect to the parameters $\{C_i\}$ and subtracting the energy of Ψ^N , gives the EKT equations as a generalized eigenvalue problem,

$$\mathbf{FC} = \mathbf{\Gamma C}\nu \quad (6)$$

where ν are the EKT IPs and the metric matrix $\mathbf{\Gamma}$ is the 1-RDM with the occupation numbers along the diagonal and zeros in off-diagonal elements. The transition matrix elements are

Figure 1: Potential energy curve of P_2 obtained at the PNOF5/cc-pVTZ level of theory.

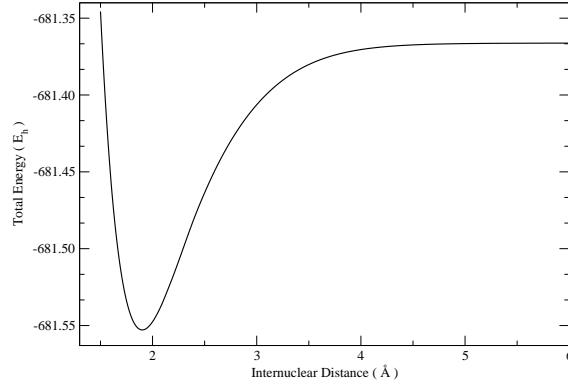
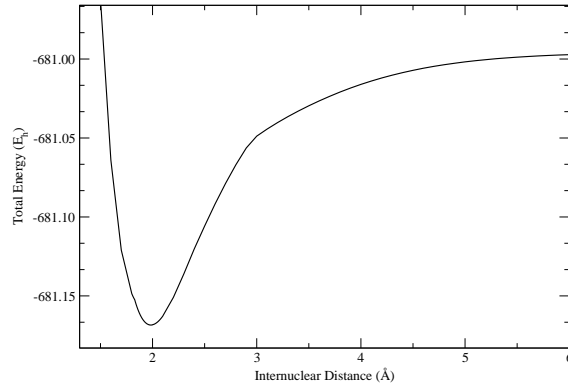


Figure 2: Potential energy curve of P_2^+ obtained at the PNOF5(P_2)+EKT/cc-pVTZ level of theory.



given by

$$F_{ji} = \langle \Psi^N | \hat{a}_j^\dagger [\widehat{\mathcal{H}}, \hat{a}_i] | \Psi^N \rangle \quad (7)$$

Considering a spin-restricted theory, it is not difficult to obtain the transition matrix elements $F_{qp} = -\lambda_{qp}$, being $\{\lambda_{qp}\}$ the set of symmetric Lagrange multipliers associated with the orthonormality of natural orbitals. Equation (6) can be transformed by a canonical orthonormalization using $\mathbf{\Gamma}^{-1/2}$. Hence, the diagonalization of the matrix ν with the elements

$$\nu_{qp} = -\frac{\lambda_{qp}}{\sqrt{n_q n_p}} \quad (8)$$

yields IPs as eigenvalues.

One test of the reliability of this procedure constitutes the prediction of the first IPs at the equilibrium and dissociation limit, which correspond to the dimer and atom species,

Table I: Comparison with the experimental values of the equilibrium bond length (R_e , in Å), dissociation energy (D_e , in kcal/mol), harmonic vibrational frequency (ω_e , in cm^{-1}), first-order ($\omega_e x_e$, in cm^{-1}) and second-order ($\omega_e y_e$, in cm^{-1}) anharmonicity constants. Properties were calculated at the PNOF5/cc-pVTZ level of theory.

	PNOF5					Experiment [25, 26]				
	R_e	D_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	R_e	D_e	ω_e	$\omega_e x_e$	$\omega_e y_e$
P_2	1.901	117.1	783.3	2.912	-0.0178	1.893	118.0	780.8	2.835	-0.0046
P_2^+	1.985	108.3	692.8	-3.951	0.8423	1.986	115.9	672.2	2.740	-

respectively. PNOF5-EKT predicts a value of 10.57 eV for P_2 , which reproduces satisfactorily the experimental vertical ionization energy of 10.62 eV, whereas the calculated IP for P atom is 10.08 eV, which underestimates in 0.4 eV the experimental mark [25]. In the case of P_2 , the experimental adiabatic ionization energy is 10.53 eV [25].

The potential energy curve obtained for the cation P_2^+ using the cc-pVTZ is shown in Fig. 2. Note that the proposed $E(P_2)$ +EKT methodology affords a proper dissociation curve. The equilibrium bond length R_e is found to change significantly from 1.901 Å for neutral P_2 to 1.985 Å for the positive ion, in excellent agreement with the experimental value of 1.986 Å [25]. On the other hand, the $E(P_2)$ +EKT calculations slightly underestimate the dissociation energy for P_2^+ in 7.6 kcal/mol with respect to the experimental value of 115.9 kcal/mol [25, 26]. This result agrees with the mentioned above underestimation of the IP for atomic species obtained using the EKT at the dissociated neutral dimer.

In Table I, selected electronic properties, including bond lengths, dissociation energies, harmonic vibrational frequencies and the anharmonicity constants can be found for both potential energy curves. The good quality of the resultant potential energy curve for P_2 is illustrated by the nice agreement with the experimental marks of the harmonic vibrational frequency and the anharmonicities. Conversely, PNOF5+EKT overestimates the harmonic vibrational frequency for the cation in 22.6 cm^{-1} .

In P_2^+ , the obtained value for the anharmonicity constant ($\omega_e x_e$) deserves special attention. In fact, there is a discontinuity in the derivative of the potential energy with respect to the internuclear distance around 3 Å. This behavior is due to the change in the solutions passing from the equilibrium region to the dissociated molecule in the neutral species, which leads

finally to a wrong value of $\omega_e x_e$ in the calculated potential energy curve for the ion through the EKT.

In summary, the calculation of potential energy curves for P_2 and P_2^+ has been achieved solely from an appropriate 2-RDM that leads to a strictly N-representable NOF for the neutral dimer. The agreement with accessible experimental data is found to be quite satisfactory without recourse to relevant wavefunctions.

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